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The main thrust of the research initiative conducted under this contract was the study of supercritical fluid solvation and separation processes under extreme solvent conditions. The specific areas of research included studies of the cybotactic region of select probe molecules, determination of stationary phase solvation in supercritical fluid chromatography and extension of supercritical fluids to the separation of highly polar (charged) solute molecules.

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FINAL REPORT

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ARO PROPOSAL NUMBER: 23921-CH

PERIOD COVERED BY REPORT: Final Report 1 Aug 87 - 31 Jul 90

TITLE OF PROPOSAL: The Development of Improved Capillary Supercritical Fluid Chromatography and Mass Spectrometry

CONTRACT OR GRANT NUMBER: DAAL03-87-K-0042

NAME OF INSTITUTION: Battelle-Pacific Northwest Laboratories

AUTHOR(S) OF REPORT: Clement R. Yonker and Richard D. Smith

FOREWORD:

Supercritical fluids have been demonstrated to be flexible solvents in analytical separations, extractions, and reaction processes. The reasons arise from a combination of their unique physicochemical properties. The solvent characteristics of a supercritical fluid are comparable to both liquids and gases. The mass transfer characteristics are similar to a gas (low viscosity), while the density can approach those observed for liquids. Both of these parameters are easily controlled as a function of pressure and/or temperature, which leads to enhanced efficiency in extraction and separation processes for thermally labile and/or non-volatile components.

The main thrust of the research initiative conducted under this contract was the study of supercritical fluid solvation and separation processes under extreme solvent conditions. The specific areas of research included studies of the cybotactic region of select probe molecules, determination of stationary phase solvation in supercritical fluid chromatography and extension of supercritical fluids to the separation of highly polar (charged) solute molecules.

The cybotactic region consists of the local solvent molecules whose structure and composition is determined by the presence of the solute molecule. Therefore, the spectroscopic study of this region leads to specific physicochemical information on the effect of temperature, pressure and density on the local density and local composition about the solute molecule. Investigation of thermochromic shifts in the electronic spectra of 2,4-nitroanisole at constant density and constant pressure was undertaken. One of the advantages of thermochromic studies in supercritical fluids is the ability to hold the fluid density constant while the variable, temperature, is changed. These studies demonstrated that the increased thermal energy added to the system had an impact on the local solvent environment about the solute molecule. The thermochromic shifts seen were not as large as previously studied solvatochromic shifts, but they were significant, and lead to a greater understanding of the relationship between internal energy of the system and the cybotactic region about the solute molecule.

The investigation of the solvation state of the stationary phase in supercritical fluid chromatography can lead to a better fundamental understanding of the chromatographic retention mechanism under extreme solvent conditions. Studies in this area involved the use of mass spectrometric tracer pulse chromatography (MSTPC). The absorption of mobile phase components from both pure and binary supercritical fluids into the stationary phase can be readily determined as a function of pressure, temperature, density and composition. Information obtained from MSTPC experiments can lead to a better understanding of the role of

stationary phase solvation on the chromatographic retention mechanism. Results demonstrated that the amount of a binary modifier (2-propanol) sorbed into the bonded stationary phase decreased with increasing fluid density (i.e. pressure). At higher densities (pressures), the concentration of 2-propanol sorbed into the stationary phase apparently approaches that of 2-propanol in the bulk mobile phase. At lower mobile phase densities, 2-propanol partitioned more extensively into the stationary phase. The sorption isotherm for CO_2 showed a maxima in the reduced density region of 0.5 to 1.0, which is consistent with studies reported in the literature for other systems. The amount of CO_2 absorbed into the stationary phase was determined to be less than that seen for 2-propanol in the binary supercritical fluid. The MSTPC technique presents an important opportunity for studying the affect of stationary phase solvation on the chromatographic retention mechanism under extreme conditions with polar solvent systems.

The extension of supercritical fluid separation methodologies to polar compounds entails the use of novel separation strategies. These strategies involve the use of very polar binary solvent modifiers in the supercritical fluid, the introduction of a specific secondary equilibrium process that enhances solute solubility in the supercritical fluid (e.g. micelles), or the direct use of polar fluids, such as, water, methanol or ammonia. Each strategy has its own particular draw-backs and limitations. Most highly polar compounds are charged or can be ionized to some extent, it was decided to develop a novel separations technology based on supercritical fluid capillary electrophoresis (SCE). This decision was predicated on the reported investigations of electrochemical processes occurring at electrode surfaces in supercritical water and other fluid systems. These reports pointed to the fact that a sustained current could be carried by a background electrolyte in a supercritical fluid which is necessary for SCE. Initial investigations where undertaken using supercritical methanol (T_c=240°C and P_c=78.9 atm) over a temperature range of 25-280°C and a pressure range of 1-280 atm. Results demonstrated the viability and utility of SCE to separate highly polar, charged systems in supercritical fluids. This technique could potentially be used to enhance resolution, separation efficiency and separation speed in mass transfer limited systems. Of major interest is the physicochemical study of the surface double layer as a function of pressure and temperature. Specific changes in the zeta potential of the capillary surface and probe molecule with density can also be studied. The effects on the electrophoretic and electroosmotic mobilities by changing fluid viscosity and dielectric constant, and the electrostriction of solvent about an ion in a supercritical fluid can be investigated. Studies of these types should be amenable with SCE, leading to a better understanding of the physicochemical parameters governing polar solute separation under extreme conditions.

The most important results obtained during this three-year period of study were: (1) the ability to spectroscopically study the cybotactic region about the solute molecule in a supercritical fluid under various conditions of temperature, pressure and density; (2) the understanding of the affect of pressure, temperature and density on the absorption isotherm of mobile phase components in the stationary phase in supercritical fluid chromatography; and (3) the development and initial studies of highly polar solute separations under extreme fluid conditions using SCE. These various studies have contributed to the further understanding of solvation and separations processes in supercritical fluids. Detailed descriptions of these developments have been given in papers prepared for publication during the course of this program.

A list of manuscripts published during this contract period is as follows:

C.R. Yonker and R.D. Smith "Thermochromic Shifts in Supercritical Fluids", J. Phys. Chem. 93 (1989) 1261-1264.

R.D. Smith, B.W. Wright and C.R. Yonker "Supercritical Fluid Chromatography: Current Status and Prognosis", Anal. Chem. 60 (1988) A1323-A1336.

C.R. Yonker and R.D. Smith "Sorption Isotherms of Mobile Phase Components in Capillary Supercritical Fluid Chromatography", J. Chromatogr. 505 (1990) 139-146.

C.R. Yonker and R.D. Smith "High Pressure and Supercritical Capillary Electrophoresis", J. Chromatogr. accepted for publication.

C. R. Yonker and R. D. Smith "Sorption Isotherms in Supercritical Fluid Chromatography: A Review", J. Chromatogr., in preparation.

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